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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

Zbyslaw R. Owczarczyk, et al

ORGANIC ELEMENT FOR  
ELECTROLUMINESCENT DEVICES

Serial No. 10/813,833

Filed 31 March 2004

Group Art Unit: 1774

Examiner: Dawn L. Garrett

Commissioner for Patents  
P.O. Box 1450  
Alexandria VA 22313-1450

Sir:

**DECLARATION UNDER RULE 132**

The undersigned, Viktor V. Jarikov, of Monroe County, New York, declares that:

He has received the degree of M.S. in Chemical Technology from Moscow University for Chemical Technology of Russia, Moscow, Russia and the degree of Ph.D. in Photochemical Sciences from Bowling Green State University, Bowling Green OH;

Since January 2000, he has been engaged in research pertaining to Organic Light-Emitting Diode technology focusing particularly on device lifetime issues and has many patents and several publications on the subject;

He is an inventor in the above-captioned patent application;

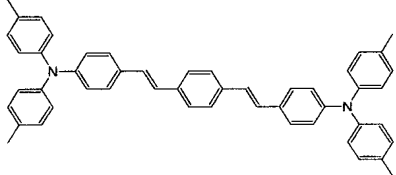
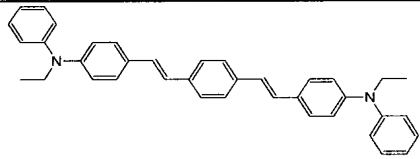
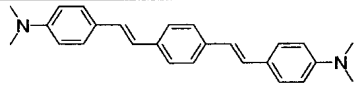
He has reviewed the outstanding Office Action and any applicable cited references.

The following experiments and calculations were performed in accordance with the ordinary course of business of Eastman Kodak Company.

In terms of OLED operating lifetime, compounds having triarylamine fragment(s) have been found to be much more stable than those

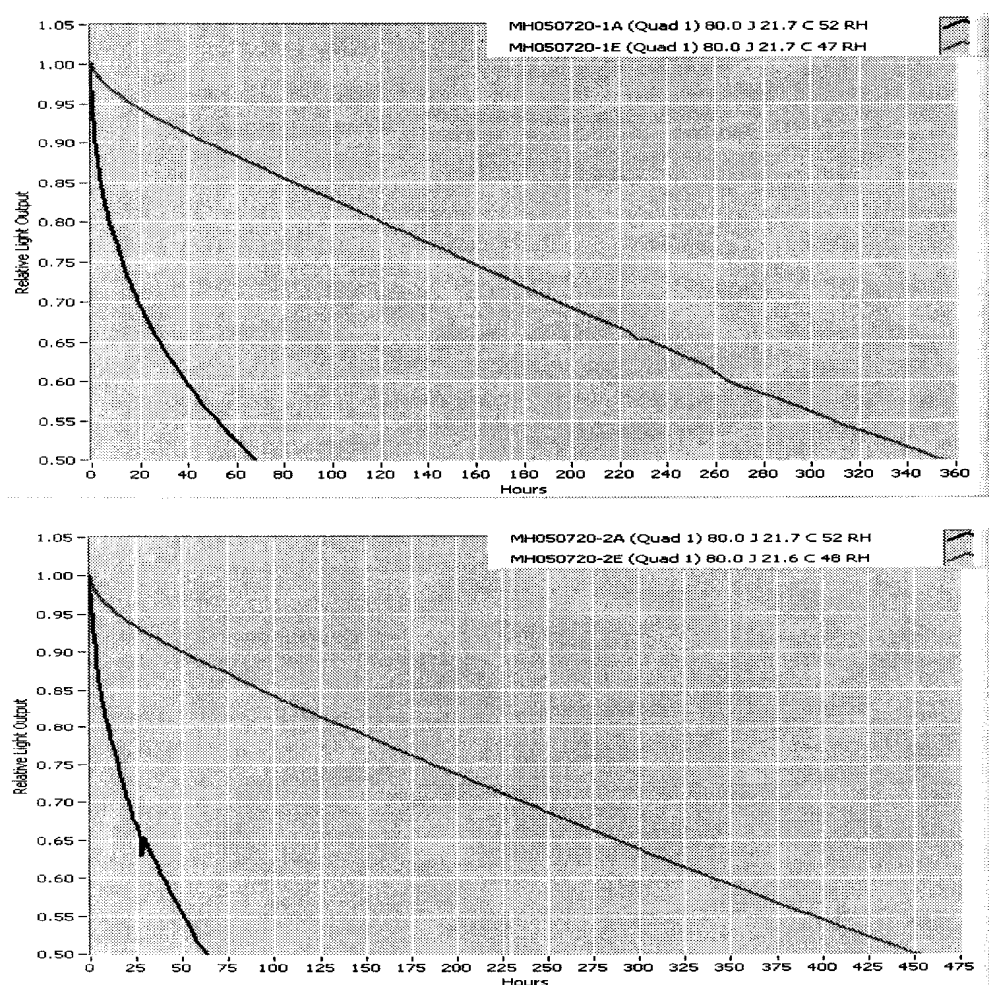
having alkyl substituents on the nitrogen atom. It appears that the root cause of this difference involves the presence of the relatively weak nitrogen–alkyl bond(s), which turns out to typically be the weakest bond in an OLED compound. A reasonable hypothesis of the degradation mechanism involves a homolysis of the nitrogen–alkyl bond, which may occur in the excited singlet state. For instance, the bond dissociation energy (BDE) of the model  $\text{Ph}(\text{CH}_3)\text{N}-\text{CH}_3$  bond is  $\sim 71$  kcal/mol, which corresponds to the energy of a 403-nm photon.<sup>1</sup> This energy is quite comparable with the excited singlet state energies of blue fluorophores (hosts and dopants) used in OLEDs, which means that the homolytic bond cleavage is energetically feasible. The primary products of the homolysis, i.e., radicals, can engage in follow-up reactions and produce species that would act as luminescence quenchers and nonradiative recombination centers/charge traps.<sup>2</sup> One representative example is furnished by the comparison of the well-known in the art, blue- and blue-green-emitting styrylamine dopants bearing all aromatic *N*-substituents versus the 5–10 times less stable *N*-alkylated analogs (concrete examples are cited below).

The first following compound is well known in the art as a blue-green-emitting styrylamine dopant. The other two are alike except for the presence of one or more alkyl groups on the nitrogen atom.

Bis(ditolylaminostyryl)benzene (BDTASB)	
PEASB	
DMASB	

The EL properties of the BDTASB analog having two *N*-phenyl-*N*-ethylamino groups instead of the two di(*p*-tolyl)amino groups (PEASB) are close to those of BDTASB except for device lifetime. The EL spectrum of the

NPB|TBADN+3%PEASB|Alq cell is very close to that of BDTASB but slightly bluer, peaking at 464 nm versus 472 nm for BDTASB.  $CIE_{x,y}$  are 0.15, 0.23 and the EQE is 3.8% (6.0 cd/A) at 20 mA/cm<sup>2</sup> and 5.7 V versus  $CIE_{x,y}$  of 0.15, 0.30 and EQE of 3.8% for the NPB|TBADN+3%BDTASB|Alq control device. However, the half-life of the PEASB device is only ~600 h versus ~3000 h for the BDTASB control cell, both at 20 mA/cm<sup>2</sup> (see upper graph where the rightmost curve belongs to the BDTASB device and the leftmost curve belongs to the PEASB device; both operated at 80 mA/cm<sup>2</sup>).

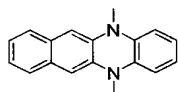


The case of the closely related 1,4-*bis*(4-dimethylaminostyryl)benzene (DMASB) is analogous. The EL spectrum of the

NPB|TBADN+3%DMASB|Alq cell is close to that of BDTASB except it is, again, slightly bluer (464 nm).  $CIE_{x,y}$  are 0.16, 0.28 and the EQE is slightly lower, 3.0% (5.5 cd/A) at 20 mA/cm<sup>2</sup> and 6.5 V. The half-life of the DMASB device is only ~420 h versus ~3800 h for the BDTASB cell (NPB|TBADN+3%BDTASB|Alq), both at 20 mA/cm<sup>2</sup>. See lower graph where the rightmost curve belongs to the BDTASB control device and the leftmost curve belongs to the DMASB device; both operated at 80 mA/cm<sup>2</sup>).

The BDE of the nitrogen–ethyl bond, that is the weakest bond in PEASB, was calculated. The calculations can be described as "B3LYP/6-311++G\*\*//B3LYP/MIDI! with zero-point energy corrections calculated using B3LYP/MIDI!". The calculation method used gives results that correlate very well ( $R^2=0.966$ ) with experimental BDEs as proven over a large set of bonds. The calculated BDE of the nitrogen–ethyl bond in PEASB is 62.5 kcal/mol, which is significantly lower than the calculated BDE of the corresponding nitrogen–tolyl bond of 80.1 kcal/mol in BDTASB. Thus, a reasonable explanation for the inferior lifetime of PEASB and DMASB compared to BDTASB involves the inclination of the former two dopants to undergo a homolytic cleavage of the nitrogen–alkyl bond in the excited singlet state, which leads to the formation of luminescence-reducing degradation products inside an operating device.

Another example of the destabilizing effect of the presence of the nitrogen–alkyl fragment in an LEL material is given by 5,12-dimethylbenzo[*b*]phenazine (DMBP).



DMBP

It emits at 430 nm in solution. However, upon doping of 0.3–20% of DMBP into the LEL of the NPB|TBADN|Alq device, the blue emission of TBADN is replaced by a wide EL band, peaking at ~550 nm (FWHM ~105 nm) attributable to the TBADN-DMBP exciplex.  $CIE_{x,y}$  are ~0.40, ~0.48. The EQE is 2.5% at 20 mA/cm<sup>2</sup> and 7 V. The half-life is reduced from ~1300 h at 20 mA/cm<sup>2</sup>

for the undoped control cell to ~600 h at 0.1–2% DMBP and more so at higher concentrations. The reason for instability again appears to involve the relatively weak nitrogen–alkyl bonds.

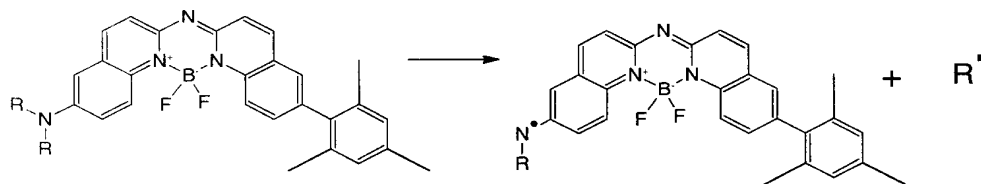
The picture is similar with doping DMBP into NPB, as in NPB|NPB+DMBP|Alq: the lifetime gradually decreases with the increasing dopant concentration from ~1300 h at 1% down to 250 h at 20% versus ~2500 h for the undoped control device, all at 20 mA/cm<sup>2</sup>.

A genuine DMBP EL can be observed in the NPB|CBP+DMBP|BAIq|Alq device structure. At the optimal doping level of 1% of DMBP, the EL spectrum peaks at 444 and 460 nm (FWHM 68 nm, CIE<sub>x,y</sub> 0.16, 0.13). The EQE is 1.7% (vs. 0.8% for the undoped control cell) and the half-life is 65 times shorter than that of the undoped control cell, ~2 h vs. 130 h at 20 mA/cm<sup>2</sup>.

The EL behavior of the 2,3-dimethylated derivative and of the 1-aza derivative of DMBP is nearly identical to that of the parent compound in both the TBADN and CBP hosts.

In contrast, when the alkyl groups of DMBP are replaced by aryls, as in the 5,12-di(*p*-tolyl)-2,3-dimethyl derivative of DMBP (DTMBP), the instability issue disappears. Thus, e.g., the TBADN-DTMBP exciplex is ~6.5 times longer-lived (~4000 h at 20 mA/cm<sup>2</sup>). This, again, points to the *N*-alkyl groups as the source of the instability.

We used the same calculation method as described above to compute a bond dissociation energy corresponding to the following reaction, which is applicable to the compounds of the present invention:



where R = ethyl or phenyl

As expected, the weakest bond in this molecule (R = ethyl) is the nitrogen-ethyl bond and its calculated BDE is 69.9 kcal/mol, which is significantly lower than the calculated BDE of the corresponding nitrogen-phenyl bond (R = phenyl) of 83.2 kcal/mol. Thus, it appears that the inventive dopants bearing alkyl substituents would be far less stable in an operating device than the claimed dopants of the present invention containing tertiary aromatic amine fragments.

In further support, the related alkoxy-substituted LEL materials are also unstable. For example, the methoxy-substituted styrylamine dopants (having diarylamino groups) are invariably less stable by at least an order of magnitude than conventional styrylamine dopants. Again, the reason behind this observation is believed to involve the relatively weak oxygen-alkyl bonds: e.g., the BDE of the model PhO-CH<sub>3</sub> bond is ~65 kcal/mol, which corresponds to the energy of a 440-nm photon.<sup>1,3,4</sup> Many examples of the destabilizing effect of the alkoxy substituents can be furnished on Examiner's request.

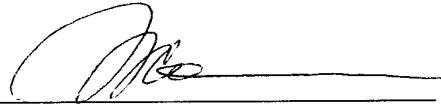
Sources:

- (1) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, FL, USA, 2002.
- (2) Kondakov, D. Y.; Lenhart, W. C.; Nichols, W. F. *J. Appl. Phys.* **2007**, *101*, 024512.
- (3) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of photochemistry*; Dekker: New York, 1993.
- (4) Blanksby, S. J.; Ellison, G. B. *Accounts of Chemical Research* **2003**, *36*, 255-263.

The foregoing demonstrates that the use of compounds having triarylamine fragment(s) provides an unexpectedly superior device lifetime compared to the same compounds but having *N*-alkyl or alkoxy fragment(s).

The undersigned declares further that all statements made herein of the undersigned's own knowledge are true and all statements made on information and belief are believed to be true. These statements are made with

the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

A handwritten signature in black ink, appearing to read 'V. Jarikov', is written over a horizontal line.

Viktor V. Jarikov

Date: June 21, 2007